Inter (Part-I) 2021

Chemistry	Group-II	PAPER: I
Time: 2.40 Hours	(SUBJECTIVE TYPE)	Marks: 68

SECTION-I

2. Write short answers to any EIGHT (8) questions: **(16)**

(i) Define stoichiometry. Give two assumptions for stoichiometric calculations. Justify it.

Ans Stoichiometry is the branch of chemistry which tells us the quantitative relationship between reactants and products in a balanced chemical equation.

To perform stoichiometric calculations, following assumptions are necessary:

(i) All the reactants are completely converted into the products.

(ii) No side reaction occurs.

(ii) How percentage yield is calculated?

Ans A chemist is usually interested in the efficiency of a reaction. The efficiency of a reaction is expressed by comparing the actual and theoretical yields in the form of percentage (%) yield.

$$\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

(iii) Define Avogadro's number. Give one example.

Ans Avogadro's number is the number of atoms, molecules and ions in one gram atom of an element, one gram molecule of a compound and one gram ion of a substance, respectively.

To understand Avogadro's number, let us consider the following quantities of substances:

1.008 g of hydrogen = 1 mol of H = 6.02×10^{23} atoms of H

23 g of sodium = 1 mol of Na = 6.02×10^{23} atoms of Na

238 g of uranium = 1 mol of U = 6.02×10^{23} atoms of U

This number, 6.02×10^{23} is the number of atoms in one mole of the element.

(iv) Differentiate between stationary phase and mobile phase in chromatographic technique.

Ans

Stationary Phase	Mobile Phase
1. Stationary phase adsorbs the mixture under separation in chromatography.	1. Mobile phase, while passing over the stationary phase, competes with it for the constituents of the mixture.
2. It may be a solid or a liquid supported on a solid.	2. It may be a liquid or a gas.

(v) What is ether extraction?

Ans A method of extracting a desired component from the solution by shaking it with a second liquid in which component is more soluble and which is immiscible with the first liquid is called solvent extraction.

The most common laboratory example of solvent extraction is ether extraction. This is used to separate the products of organic synthesis from water.

The technique is particular useful when the product is volatile or thermally unstable.

(vi) Derive Avogadro's law from KMT.

Ans Avogadro's Law:

Consider two gases 1 and 2 at the same pressure P and having the same volume V. Their number of molecules are N_1 and N_2, masses of molecules are m_1 and m_2 and mean square velocitieis are $\bar{c}_1^2$ and $\bar{c}_2^2$, respectively. Their kinetic equations can be written as follows:

$$PV = \frac{1}{3} m_1 N_1 \bar{c}_1^2 \quad \text{for gas (1)}$$

$$PV = \frac{1}{3} m_2 N_2 \bar{c}_2^2 \quad \text{for gas (2)}$$

Equalizing $\frac{1}{3} m_1 N_1 \bar{c}_1^2 = \frac{1}{3} m_2 N_2 \bar{c}_2^2$

Hence $m_1 N_1 \bar{c}_1^2 = m_2 N_2 \bar{c}_2^2$ ... (i)

When the temperature of both gases is the same, their mean kinetic energies per molecule will also be same, so

$$\frac{1}{2} m_1 \bar{c}_1^2 = \frac{1}{2} m_2 \bar{c}_2^2$$

or $\quad m_1 \bar{c}_1^2 = m_2 \bar{c}_2^2$ $\qquad$ ... (ii)

Divide equation (i) by (ii),

$$N_1 = N_2$$

Hence equal volumes of all the gases at the same temperature and pressure contain equal number of molecules, which is Avogadro's law.

(vii) Why the graph plotted between pressure and volume moves away from pressure axis at higher temperature?

Ans The reason is that at higher temperature, the volume of the gas has increased. Similarly, if we increase the temperature further, make it constant and plot another isotherm, it further goes away from the axis.
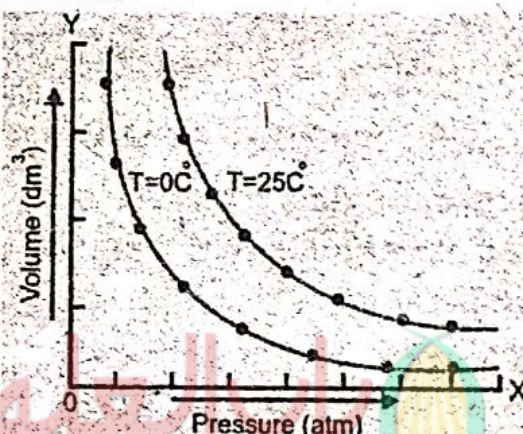

Fig. Isotherms of a gas at different temperatures.

(viii) Calculate SI unit of 'R' gas constant.

Ans Using SI units of pressure, volume and temperature in the general equation, the value of R is calculated as follows. The SI units of pressure are Nm^{-2} and of volume are m^3. By using Avogadro's principle

$$1 \text{ atm} = 760 \text{ torr} = 101325 \text{ Nm}^{-2}$$
$$1 \text{ m}^3 = 1000 \text{ dm}^3$$

$n = 1$ mole

$T = 273.16$ K

$P = 1$ atm $= 101325$ Nm^{-2}

$V = 22.414$ dm$^3 = 0.022414$ m^3

Putting their values, along with units.

$$R = \frac{PV}{nT} = \frac{101325 \text{ Nm}^{-2} \times 0.02241 \text{ m}^3}{1 \text{ mol} \times 273.16 \text{ K}}$$

$$R = 8.3143 \text{ NmK}^{-1} \text{ mol}^{-1}$$
$$= 8.3143 \text{ JK}^{-1} \text{ mol}^{-1} \quad (1 \text{ Nm} = 1 \text{ J})$$

Since 1 cal. = 4.18 J

So, $$R = \frac{8.3143}{4.18} = 1.989 \text{ cal K}^{-1} \text{ mol}^{-1}$$

Keep in mind that, wherever the pressure is given in Nm^{-2} and the volume in m^3, then the value of R used must be 8.3143 $JK^{-1} mol^{-1}$.

(ix) Why does pilots feel uncomfortable breathing at high altitude?

Ans At higher altitudes, the pilots feel uncomfortable breathing because the partial pressure of oxygen in the un-pressurized cabin is low, as compared to 159 torr, where one feels comfortable breathing.

(x) State Raoult's law. Give one mathematical expression.

Ans Raoult's law can be defined in these ways:

The vapour pressure of a solvent above a solution is equal to the product of the vapour pressure of pure solvent and the mole fraction of solvent in solution.

Mathematically, it can be written in equation form as follows:

$$p = p^o x_1 \qquad \qquad ... (i)$$

where p is the vapour pressure of solvent in the solution, p^o is the vapour pressure of pure solvent and x_1 is the mole fraction of solvent.

We also known that

$$x_1 + x_2 = 1 \quad (x_2 \text{ is the mole fraction of solute})$$

or $$x_1 = 1 - x_2$$

Putting the value of x_1 in equation (i)

$$p = p^o (1 - x_2)$$

or $$p = p^o - p^o x_2$$

or $$p^o - p = p^o x_2$$

or $$\Delta p = p^o x_2 \qquad \qquad ... (ii)$$

Equation (ii) gives another definition of Raoult's law. "The lowering of vapour pressure is directly proportional to the mole of fraction of solute."

(xi) Relative lowering of vapour pressure is independent of temperature. Justify this statement.

Ans The relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{\Delta p}{p^o} = X_2$$

Mole fraction of the solute is a temperature independent quantity. Mole fraction of solute is ratio of no. of moles of solute to the total no. of moles of solute and solvent. No. of moles does not depend upon temperature. Hence, relative lowering of vapour pressure is temperature independent.

(xii) Give two applications of colligative properties.

Ans The practical applications of colligative properties are numerous. The study of colligative properties has provided us with methods of molecular mass determination and has also contributed to the development of solution theory.

3.   Write short answers to any EIGHT (8) questions: (16)

(i)   What are dipole-dipole forces? Give one example.

Ans In case of HCl molecule, both atoms differ in electronegativity. Chlorine being more electronegative, develops the partial negative charge and hydrogen develops the partial positive charge. So, whenever the molecules are close to each other, they tend to line up. The positive end of one molecule attracts the negative end of the other molecule and these electrostatic forces of attraction are called dipole-dipole forces.

(ii)   Name the factors which affect the London forces.

Ans Factors which affect London forces are as follows:
1.   Polarizability.
2.   Number of atoms ina non-polar molecule.

(iii)   Cleavage of the crystals is itself anisotropic behaviour. Explain.

Ans Anisotropic crystals having different intensity of property in different directions is called cleavage. Cleavage is anisotropic property because many crystals have a specific cleavage plane. For example, mica sheets can be cleaved only parallel to length of sheet and not easily in any other direction.

(iv) Define transition temperature with two examples.

Ans It is that temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other. At this temperature, one crystalline form of a substance changes to another. Above and below this temperature, only one form exists. A few examples for those substances which show allotropy and possess a transition temperature are given below:

(i)   Grey Tin (cubic) $\underset{}{\overset{13.2^{\circ}C}{\rightleftharpoons}}$ White tin (Tetragonal)

(ii)   Sulphur S_8 (rhombic) $\underset{}{\overset{95.5^{\circ}C}{\rightleftharpoons}}$ Sulphur S_8 (monoclinic)

(v) Why cathode rays are also called as electron?

Ans The e/m value of cathode rays shows that they are simply electrons. J.J. Thomson concluded from his experiments that cathode rays consist of streams of negatively charged particles. Stoney named these particles as electrons. Thomson also determined the charge to mass ratio (e/m) of electrons. He found that the e/m value remained the same no matter which gas was used in the discharge tube.

(vi) Write down any four properties of positive rays.

Ans Following are four properties of Positive Rays:

1. They are deflected by an electric as well as a magnetic field showing, that these are positively charged.
2. These rays travel in a straight line in a direction opposite to the cathode rays.
3. They produce flashes on ZnS plate.
4. The e/m value for the positive rays is always smaller than that of electrons and depends upon the nature of the gas used in the discharge tube.

(vii) Define spectrum and name any two types of spectrum.

Ans A visual display or dispersion of the components of white light, when it is passed through a prism is called a spectrum.

Spectrum is of two types:
(i) Continuous spectrum
(ii) Line spectrum

(viii) For Azimuthal quantum number, $\ell = 2$ and $\ell = 3$, calculate the total values of magnetic quantum number (m).

Ans $\ell = 2$ d-subshell $m = 0, \pm 1, \pm 2$ (d-subshell has five degenerate orbitals)

$\ell = 3$ f-subshell $m = 0, \pm 1, \pm 2, \pm 3$ (f-subshell has seven degenerate orbitals)

(ix) How equilibrium constant (K_c) predicts direction of a reaction?

Ans The direction of a chemical reaction at any particular time can be predicted by means of [products] / [reactants] ratio, calculated before the reaction attains equilibrium. The value of [product] / [reactants] ratio leads to one of the following three possibilities:

(a) The ratio is less than K_c. This implies that more of the product is required to attain the equilibrium, therefore, the reaction will proceed in the forward direction.

(b) The ratio is greater than K_c. It means that the reverse reaction will occur to attain the equilibrium.

(c) When the ratio is equal to K_c, then the reaction is at equilibrium.

(x) Define pH. How it is helpful to know nature of solutions?

**Ans** pH is defined as the negative log of hydrogen ion concentration.

$$pH = -\log [H^+]$$

The value of pH normally varies between $0 \rightarrow 14$ at 25°C. The solution having pH 7 is neutral. The solution with pH less than 7 is acidic and that with pH more than 7 from 8 to 14 is basic.

(xi) What do you mean by order of reaction? Give two examples.

Ans **Order of reaction:** It is the sum of the exponents of the concentration terms in the rate expression of a chemical reaction.

Examples:

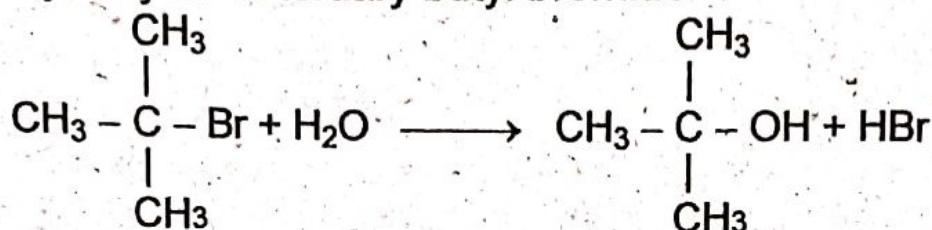1. Decomposition of nitrogen pentoxide involves the following equation:

$$2N_2O_{5(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$$
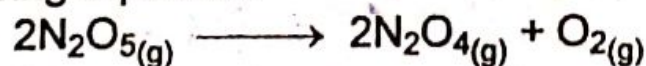
The experimentally determined rate equation for this reaction is as follows:

$$Rate = k[N_2O_5]$$

This equation suggests that the reaction is first order with respect to the concentration of N_2O_5.

2. Hydrolysis of tertiary butyl bromide

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - Br + H_2O \longrightarrow CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH + HBr$$

The rate equation determined experimentally for this reaction is:

$$Rate = k[(CH_3)_3CBr]$$

The rate of reaction remains effectively independent of the concentration of water because, being a solvent, it is present in very large excess. Such type of reactions have been named as pseudo first order reactions.

(xii) What is the effect of temperature on rate of chemical reaction? Also write Arrhenius equation.

Ans Arrhenius equation explains the effect of temperature on the rate constant of a reaction. The rate constant 'k' for many simple reactions is found to vary with temperature.

According to Arrhenius:

$$k = Ae^{-Ea/RT}$$

4. Write short answers to any SIX (6) questions: (12)

(i) Bond distance is the compromise distance between two atoms. Justify.

Ans When two atoms approach each other to form a bond, they attract each other and the energy of the system is lowered. When they reach at a certain distance, their forces of attraction are maximum. On further coming close, they start repelling each other and the energy of the system increases. Now the two atoms try to remain at a compromising distance whereas the energy of the system is minimum. This is called bond distance or compromise distance between two atoms.

(ii) Write down the two postulates of VSEPR theory.

Ans Following are two postulates of VSEPR Theory:

(i) Both the lone pairs as well as the bond pairs participate in determining the geometry of the molecules.

(ii) The electron pairs are arranged around the central polyvalent atom so as to remain at a maximum distance apart to avoid repulsions.

(iii) **Differentiate between covalent and coordinate covalent bond.**

Ans

Covalent Bond	Coordinate Covalent Bond
1. A covalent bond is formed by the mutual sharing of electrons between two atoms.	1. A coordinate covalent bond is formed between two atoms when the shared pair of electrons is donated by one of the bonded atoms.
2. Example: N_2, HCl, CH $\equiv$ CH, etc.	2. $NH_3^+ \rightarrow BF_3$.

(iv) **Draw the hypothetical orbital picture of He₂ molecule according to M.O.T.**

Ans.
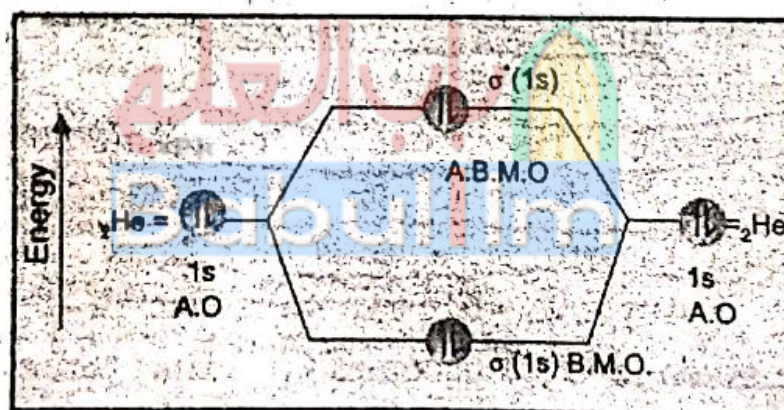
Fig. Hypothetical orbital picture of He₂ molecule.

(v) **Define enthalpy of formation with an example.**

Ans The standard enthalpy of formation of a compound is the amount of heat absorbed or evolved when one mole of the compound is formed from its elements. It is denoted by ΔH_f°. All the substances involved are in their standard physical states and the reaction is carried out under standard conditions i.e., at 25°C (298 K) and one atm. pressure. Its units are kJ mol^{-1}. For example, the enthalpy of formation, (ΔH°_f) for MgO$_{(s)}$ is –692 kJ mol^{-1}.

$$Mg_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow MgO_{(s)} \qquad \Delta H_1^o = -692 \text{ kJ mol}^{-1}$$
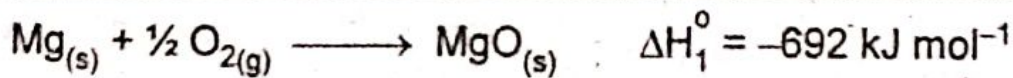
(vi) Prove $q_v = \Delta E$.

Ans Consider, a gas enclosed in a cylinder having a frictionless piston. When a quantity of heat 'q' is supplied to the system, its internal energy E_1 changes to E_2 and piston moves upwards. The change in internal energy ΔE is given by the following equation

$$\Delta E = E_2 - E_1 = q + w$$
$$\Delta E = q + w$$

In this equation, 'q' represents the amount of heat absorbed by the system and 'w' is the work done by the system in moving the piston up.

If 'w' is pressure-volume work, then the above expression assumes the following form:

$$\Delta E = q - P\Delta V \qquad \text{... (i)}$$

When the piston is kept in its original position or the volume of the gas is not allowed to change, then $\Delta V = 0$ and equation (i) will take the following form:

$$\Delta E = q_v \qquad \text{... (ii)}$$

This shows that a change in internal energy of a system, at constant volume is equal to heat absorbed by the system (q_v).

(vii) Calculate the oxidation numbers of the elements underlined: (a) $Na_2\underline{P}O_4$ (b) $H\underline{N}O_3$.

Ans (a) $Na_2\underline{P}O_4$:

2 (O.N of Na) + O.N of P + 4 (O.N of O) = 0

$$2 (+1) + P + 4 (-2) = 0$$
$$2 + P - 8 = 0$$
$$P - 6 = 0$$
$$\boxed{P = +5}$$

(b) $H\underline{N}O_3$:

O.N of H + O.N of N + 3 (O.N of O) = 0

$$+1 + N + 3(-2) = 0$$
$$+1 + N - 6 = 0$$
$$N - 5 = 0$$
$$\boxed{N = +5}$$

(viii) How salt bridge maintains the electrical neutrality in the cell? Justify.

Ans A salt bridge is a U-tube containing saturated solutions of strong electrolytes, e.g., KCl, KNO_3. It connects the two electrolytic solution. When electrochemical reaction takes place in the cell, it allows the passage of negative ions from the cathode compartment to anode compartment. As a result of that, both compartments become neutral.

(ix) What is standard hydrogen electrode (SHE)?

Ans A standard hydrogen electrode which is used as a standard is shown in Fig.

It consists of a piece of platinum foil, which is coated electrolytically with finely divided platinum black to give it a large surface area and suspended in one molar solution of HCl. Pure hydrogen gas at one atmosphere pressure is continuously bubbled into 1 M HCl solution.
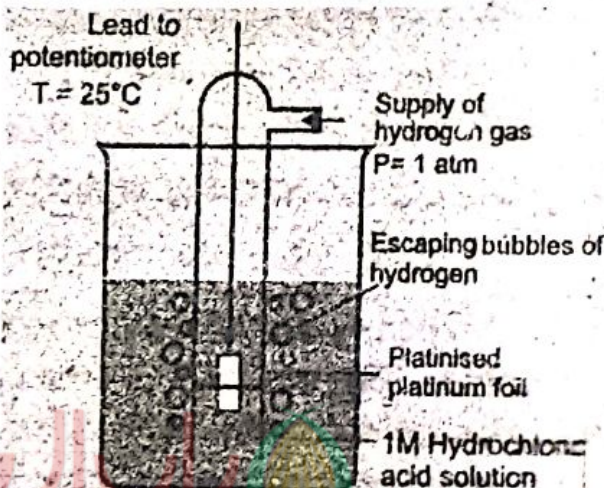
The platinum acts as an electrical conductor and also facilitates the attainment of equilibrium between the gas and its ions in solution. The potential of this electrode is arbitrarily taken as zero.

SECTION-II

NOTE: Attempt any Three (3) questions.

Q.5.(a) Calculate the number of grams of K_2SO_4 and H_2O produced when 14 gram of KOH reacts with excess of H_2SO_4 under the following equation: (4)

$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$

Ans For doing such calculations, first of all convert the given mass of KOH into moles and then compare these moles with those of K_2SO_4 with the help of the balanced chemical equation.
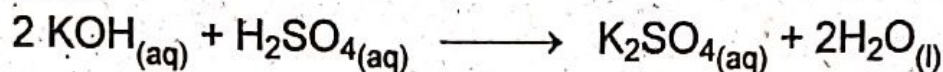
Mass of KOH = 14.0 g

Molar mass of KOH = 39 + 16 + 1 = 56 g/mol

No. of moles of KOH $= \dfrac{14.0\ g}{56\ g\ mol^{-1}} = 0.25$

Equation:

$$2\ KOH_{(aq)} + H_2SO_{4(aq)} \longrightarrow K_2SO_{4(aq)} + 2H_2O_{(l)}$$

To get the number of moles of K_2SO_4, compare the moles of KOH with those of K_2SO_4.

KOH	:	K_2SO_4
2	:	1
1	:	$\frac{1}{2}$
0.25	:	0.125

So, 0.125 mole of K_2SO_4 is being produced from 0.25 mole of KOH.

Molar mass of $K_2SO_4 = 2 \times 39 + 96$

$\qquad\qquad\qquad\qquad = 174$ g/mol

Mass of K_2SO_4 produced = No. of moles × molar mass

$\qquad\qquad\qquad\qquad = 0.125$ mol × 174 g mol^{-1}

$\qquad\qquad\qquad\qquad = 21.75$ g

To get the number of moles of H_2O, compare the moles of KOH with those of water

KOH	:	H_2O
2	:	2
1	:	1
0.25	:	0.25

So, the number of moles of water produced is 0.25 from 0.25 mol of KOH.

Mass of water produced = 0.25 mol × 18 g mol^{-1}

$\qquad\qquad\qquad\qquad = 4.50$ g

Number of molecules of water = No. of moles × 6.02×10^{23}

$\qquad\qquad\qquad\qquad = 0.25$ mol × 6.02×10^{23}

$\qquad\qquad\qquad\qquad$ molecules per mole

$\qquad\qquad\qquad\qquad = \boxed{1.50 \times 10^{23}\ \text{molecules}}$

(b) **Explain the structure of ice on the basis of hydrogen bonding.** (4)

Ans Structure of Ice:

The molecules of water have tetrahedral structure. Two lone pairs of electrons on oxygen atom occupy two corners of the tetrahedron. In the liquid state, water molecules are extensively associated with each other and these associations break and are reformed because the molecules of water are mobile. When the temperature of water is decreased and ice is formed, then the molecules become more regular and this regularity extends throughout the whole structure. Empty spaces are created in the structure. That is why, when water freezes it occupies 9% more space and its density decreases. The result is that ice floats on water. The structure of ice is just like that of a diamond because each atom of carbon in diamond is at the center of tetrahedon just like the oxygen of water molecule in ice.

The lower density of ice than liquid water at 0°C causes water in ponds and lakes to freeze from surface to the downward direction. Water attains the temperature of 4°C by the fall of temperature in the surrounding. As the outer atmosphere becomes further cold, the water at the surface becomes less dense. This less dense water below 4°C stays on the top of slightly warm water underneath. A stage reaches when it freezes. This layer of ice insulates the water underneath for further heat loss. Fish and plants survive under this blanket of ice for months.

Keeping the whole discussion in view, we are forced to believe that the pattern of life for the plants and animals would have been totally different in the absence of hydrogen bonding in water.

Q.6.(a) State Charles's law. Explain its experimental verification. (4)

Ans Charles's Law:

It is a quantitative relationship between temperature and volume of a gas and was given by French scientist J. Charles in 1787. According to this law, the volume of the given mass of a gas is directly proportional to the absolute temperature when the pressure is kept constant.

$V \propto T$ (when pressure and number of moles are constant)

$V = kT$

$$\frac{V}{T} = k$$

If the temperature is changed from T_1 to T_2 and volume changes from V_1 to V_2, then

$$\frac{V_1}{T_1} = k \quad \text{and} \quad \frac{V_2}{T_2} = k$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \qquad \text{... (i)}$$

The ratio of volume to temperature remains constant for same amount of gas at same pressure.

Experimental Verification:

Let us consider a certain amount of a gas enclosed in a cylinder fitted with a movable piston. The volume of the gas is V_1 and its temperature is T_1. When the gas in the cylinder is heated, both volume and the temperature of the gas increase.

Movable Piston

Volume = V_2
Temperature = T_2

Volume = V_1
Temperature = T_1
$\frac{V_1}{T_1} = k$
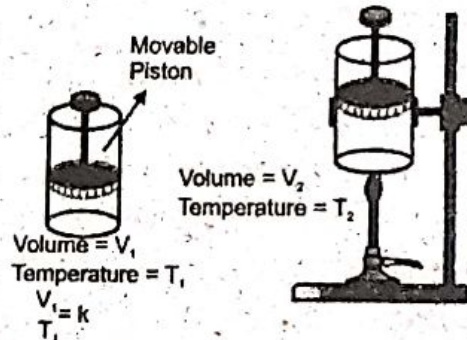
Fig. Verification of Charles's law.

The new values of volume and temperature are V_2 and T_2, respectively.

Experiment shows that

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Hence Charles's law is verified.

(b) Write down experiment that: how neutrons were discovered? (4)

Ans Chadwick discovered neutron in 1932 and was awarded Nobel prize in Physics in 1935.

Experiment:

A stream of α-particles produced from a polonium source was directed at beryllium ($_4^9Be$) target. It was noticed that some penetrating radiations were produced. These radiations were called neutrons because the charge detector showed them to be neutral, Fig. The nuclear reaction is as follows:
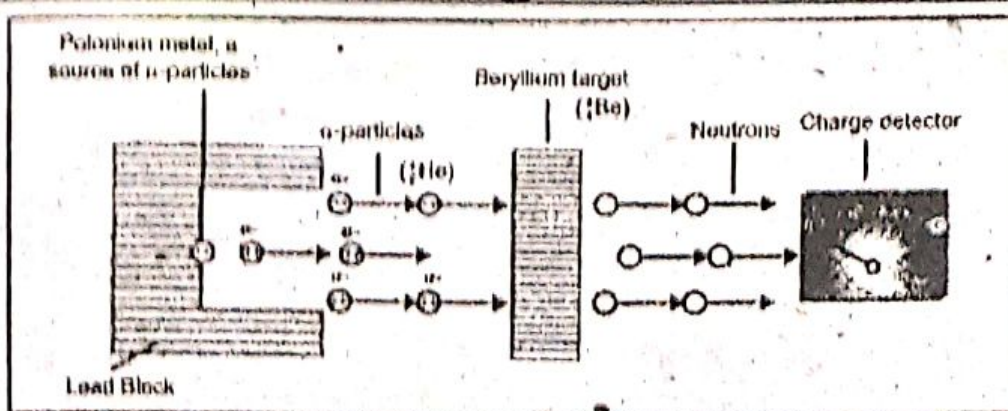
$$\underset{(\alpha\text{-particle})}{_2^4He} + {_4^9Be} \longrightarrow {_6^{12}C} + {_0^1n}$$
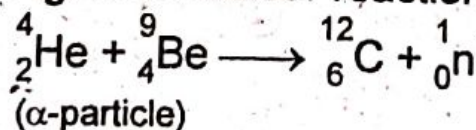
Fig: Bombardment of Be with α-particles and discovery of neutron.

Actually, α-particles and the nuclei of Be ate re-arranged and extra neutron is emitted.

Q.7.(a) Define ionization energy. Write factors affecting ionization energy and explain its trend along group. (4)

Ans ▶ Ionization Energy:

The ionization energy of an element is the minimum energy required to remove an electron from its gaseous atom to form an ion. The process is called ionization, e.g.,

$$Mg \longrightarrow Mg^+ + e^- \qquad \Delta H = 738 \text{ kJ mol}^{-1}$$

In the gaseous phase, the atoms and ions are isolated and are free from all external influences. Thus, the ionization energy is the qualitative measure of the stability of an isolated atom. The first ionization energies of elements are given in table.

Table: First Ionization energies, electron affinities and electronegativities values of elements.

Factors Influencing the Ionization Energies:

It is observed that the ionization energies of atoms depend upon the following factors:

(i) Atomic radius of atom

(ii) Nuclear charge or proton number of the atom

(iii) Shielding effect of inner electrons

(iv) Nature of orbital

Variation of Ionization Energy in the Periodic Table:

In the periodic table, the ionization energies increase from left to right in a period with the increase in the proton number, until a maximum value is reached at the end of the period. This may be explained in terms of the periodicity of the electronic configuration of elements. Each period begins with an element which has one electron in its valence shell and ends with the completion of an electronic shell. The increase in the atomic number is associated with the increase in nuclear charge which leads to a stronger force of attraction between the nucleus and the increasing number of electrons. The stronger force of attraction, ultimately results in difficult removal of electrons.

In groups, the ionization energy decreases in spite of the increase in proton number or nuclear charge. This is due to successive addition of electronic shells as a result of which the valence electrons are placed at a larger distance from the nucleus. As the force of attraction between the nucleus and the outer electron decreases with the increase in distance, the electron can be removed more easily or with less energy. Moreover, the force of attraction also decreases due to increasing shielding effect of the intervening electrons.

The ionization energies of group III-A and VI-A show abnormal trend. This can be understood from the distribution of the electrons.

(b) **Prove that** $\Delta H = q_p$. (4)

Ans To take account of increase in internal energy and accompanying work done by the gas, there is another property of the system called enthalpy or heat content. It is represented by H. In general, enthalpy is equal to the internal energy (E) plus the product of pressure and volume (PV).

$$H = E + PV$$

Enthalpy is a state function. It is measured in joules. It is not possible, to measure the enthalpy of a system in a given state. However, change in enthalpy (ΔH) can be measured for a change in the state of system. A change in enthalpy of a system can be written as:

$$\Delta H = \Delta E + \Delta(PV)$$

or $\quad\quad \Delta H = \Delta E + V\Delta P + P\Delta V$

Since, the gas is kept at constant pressure, $\Delta P = 0$

Hence, $\Delta H = \Delta E + P\Delta V$ ... (i)

In case of liquids and solids, the changes in state do not cause significant volume change, i.e., $\Delta V = 0$. For such process, ΔH and ΔE are approximately the same, i.e., $\Delta H \approx \Delta E$.

According to first law of thermodynamics:

$$\Delta E = q + w$$

If w is pressure-volume work done by the system, then:

$$w = -P\Delta V$$

So, $\quad\quad \Delta E = q - P\Delta V$

Putting the value of ΔE in equation (i), we get

$$\Delta H = q - P\Delta V + P\Delta V$$

$$\Delta H = q - \Delta P (V + V)$$

Since the pressure is constant, $\Delta P = 0$, therefore,

$$\Delta H = q_p$$

Q.8.(a) A buffer solution is prepared by mixing 0.2 M CH_3COONa and 0.5 M CH_3COOH in 1 dm^3 of solution. Calculate pH of solution. pK_a of acid is 4.74. (4)

Ans
$$[CH_3COOH] = 0.5 \text{ M}$$
$$[CH_3COONa] = 0.2 \text{ M}$$
$$pK_a = 4.74$$
$$pH = ?$$

Formula:

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

$$pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

By putting the values,

$$pH = 4.74 + \log \frac{[0.2\ M]}{[0.5\ M]}$$

$$pH = 4.74 + \log (0.4)$$

$$pH = 4.74 + (-0.4)$$

$$pH = 4.74 - 0.4$$

$$\boxed{pH = 4.34}$$

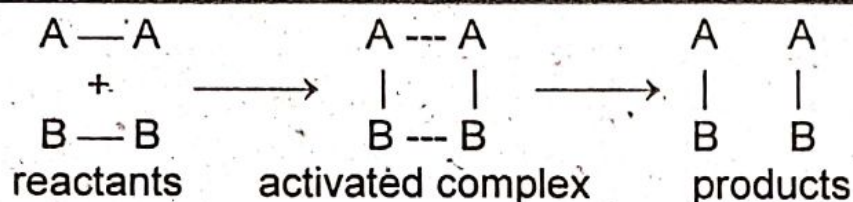| (b)	Explain energy of activation.	(4)

Ans **Energy of Activation:**

For a chemical reaction to take place, the particles atoms, ions or molecules of reactants must form a homogeneous mixture and collide with one another. These collisions may be effective or ineffective depending upon the energy of the colliding particles. When these collisions are effective, they give rise to the products otherwise the colliding particles just bounce back. The effective collisions can take place only when the colliding particles will possess certain amount of energy and they approach each other with the proper orientation.

The idea of proper orientation means that at the time of collision, the atoms which are required to make new bonds should collide with each other. The minimum amount of energy, required for an effective collision is called activation energy.

If all the collisions among the reacting species at a given temperature are effective in forming the products, the reaction is completed in a very short time. Most of the reactions, are, however, slow showing that all the collisions are not equally effective.

Let us study a reaction between molecules A_2 and B_2 to form a new molecule AB. If these molecules will have energy equal to or more than the activation energy, then upon collisions their bonds will break and new bonds will be formed. The phenomenon is shown in Fig.

$$
\begin{array}{ccccc}
\text{A—A} & & \text{A --- A} & & \text{A} \quad \text{A} \\
+ & \longrightarrow & | \quad | & \longrightarrow & | \quad | \\
\text{B—B} & & \text{B --- B} & & \text{B} \quad \text{B} \\
\text{reactants} & & \text{activated complex} & & \text{products}
\end{array}
$$

Fig. Collisions of molecules, formation of activated complex and formation of products.

Activated complex is an unstable combination of all the atoms involved in the reaction for which the energy is maximum. It is a short-lived species and decomposes into the products immediately. It has a transient existence, that is why, it is also called a transition state.

When the colliding molecules come close to each other at the time of collision, they slow down, collide and then fly apart. If the collision is effective, then the molecules flying apart are chemically different otherwise the same molecules just bounce back. When the molecules slow down just before the collision, their kinetic energy decreases and this results in the corresponding increase in their potential energy. The process can be understood with the help of a graph between the path of reaction and the potential energy of the reacting molecules.
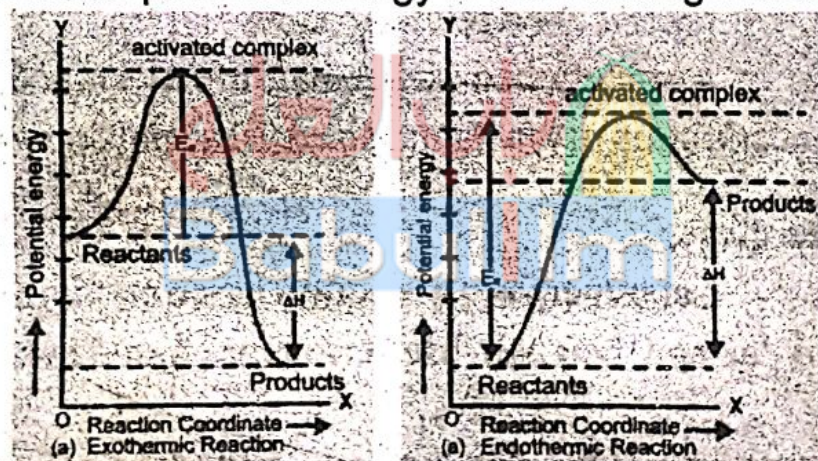
Fig. A graph between path of reaction and the potential energy of the reaction.

The reactants reach the peak of the curve to form the activated complex. E_a is the energy of activation and it appears as a potential energy hill between the reactants and the products. Only, the colliding molecules with proper activation energy, will be able to climb up the hill and give the products. If the combined initial kinetic energy of the reactants is less than E_a, they will be unable to reach the top of the hill and fall back chemically unchanged.

This potential energy diagram can also be used to study heat evolved or absorbed during the reaction. The heat of reaction is equal to the difference in potential energy of the reactants and the products. For exothermic reactions, the products are at a lower energy level than the reactants and the decrease in pontential energy appears as increase in kinetic energy of the products. For endothermic reactions, the products are at higher energy level than the reactants and for such reactions a continuous source of energy is needed to complete the reaction.

The energy of activation of forward and backward reactions is different for all the reactions. For exothermic reactions, the energy of activation of forward reaction is less than that of backward reaction, while reverse is true for endothermic reactions.

Energy of activation of a reaction provides a valuable information about the way a reaction takes place and thus helps to understand the reaction.

Q.9.(a) Define solubility curve. Explain different types of solubility curves with the help of graphs. (4)
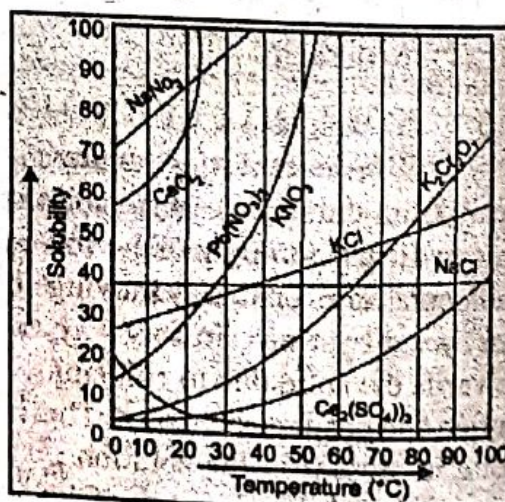
Ans Solubility Curves:

Temperature has a marked effect on the solubility of many substances. A graphical representation between temperature and solubility of solution is called solubility curves.

There are two types of solubility curves.

(a) Continuous Solubility Curves:

Continuous solubility curves don't show sharp breaks anywhere. According to Fig., $KClO_3$, $K_2Cr_2O_7$, $Pb(NO_3)_2$, and $CaCl_2$ are showing continuous solubility curves. The solubility curves of KCl, NaCl and $NaNO_3$ give the straight lines, NaCl shows a very small change of solubility from 0°C to 100°C increase of temperature.

Fig. Continuous solubility curves.

$Ce_2(SO_4)_3$ shows the exceptional behaviour whose solubility decreases with the increase in temperature and becomes constant from 40ºC onwards. Anyhow, it shows continuous solubility curve.

(b)   Discontinuous Solubility Curves:

Sometimes, the solubility curves show sudden changes of solubilities and these curves are called discontinuous solubility curves. The best examples in this reference are $Na_2SO_4.10H_2O$, $CaCl_2.6H_2O$. Actually, these curves are combination of two or more solubility curves. At the
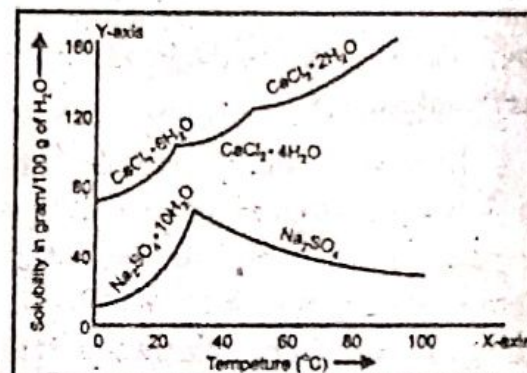

Fig. Discontinuous solubility curves.

break, a new solid phase appears and another solubility curve of that new phase begins. It is the number of molecules of water crystallization which changes and hence solubility changes, Fig.

(b)   Describe electrochemical series. Give its three applications. (4)

Ans   For Answer see Paper 2016 (Group-II), Q.9.(b).